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An ALD Etch-back Method to Fabricate High Aspect Ratio Nanopillar Arrays for Photonic Crystal Sensors

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Abstract

An IC-compatible technique for photonic crystal sensors is presented here to fabricate dense arrays of high aspect ratios nanopillars, which are made of extremely hard materials that are difficult to shape, such as TiO_2. This technique, called Atomic layer deposition ARrays Defined by Etch-back technique (AARDE), can significantly reduce direct bombardment on the functional surfaces and allows the precise control of the size of the densely spaced high pillars. A case study of an array of 1µm pitch and 1.7µm high TiO_2 pillars is investigated. Starting from 145 nm radius Si rods, the pillars are coated with a 78 nm thick ALD TiO_2 layer and subsequently uncapped by a short time plasma etching. The exposed Si cores are then removed and a second ALD deposition is used to refill the opened holes and extend the pillar radius to the desired value.

Keywords: photonic crystal sensors; ALD; high aspect ratio; hard materials

1. Introduction

A photonic crystal is a lattice-like material in which different dielectric constants vary periodically [1]. By carefully designing and constructing the photonic crystals, one can control light propagating in certain directions with specified frequencies. The interesting property of photonic crystals is that a slight change in the refractive index of the medium will lead to a sharp change in transmission of the light in certain wavelength ranges. This feature is a clear advantage for sensing operation since it is simple to detect. Fig. 1 shows a schematic example for sensing applications. The photonic crystal waveguide is formed by a triangular lattice of rods in which one row of rods is removed. Such rods should have a relatively high refractive index compare to the fluid (gas or liquid) that to be detected. The index difference between the rods and the fluid, the size of the rods and the geometry of the lattice determine the band gap of the photonic crystal, and hence, the working wavelength ranges of the device. When one kind of fluid flows into the properly designed photonic crystal sensor, it can be distinguished by the transmittance contrast.

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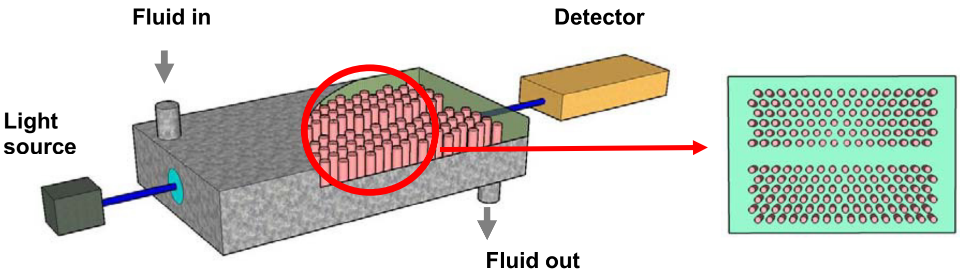

Fig. 1. Schematic drawing of the photonic crystal sensor and its functional waveguide.

Because of its unique characteristics, such as high refractive index, transparent in both visible and UV regions and exceptional chemical stability, titanium dioxide is a promising material which is widely used in optical coatings, antireflection coatings, optical waveguides and optical waveguides, etc [2]-[4]. However, this rigid and stable material is difficult to etch into dense and high aspect ratio structures. Generally, very high power and long time plasma etching is needed to form the patterns [5]. Such process often harms the quality of the functional sidewalls and requires another more stable material as the mask material for the fine structures. Therefore, it is of importance to find a better way to shape the TiO_2 nanostructures.

Among all deposition techniques, atomic layer deposition (ALD) allows precise and simple thickness control, excellent conformity along the substrates, high uniform thickness across the whole wafer and the ability to deposit films into ultra-high-aspect-ratio nanopores [6]-[8].

Instead of direct etching, an alternative method to fabricate high aspect ratio TiO_2 nanopillars is proposed here. This IC-compatible method, called ALD ARrays Defined by Etch-back technique (AARDE), allows an easy control of the size of the densely spaced high pillars.

2. Method and experimental

Fig. 2 illustrates the main process steps of the AARDE technique. The idea was to make use of Si to form the high aspect ratio and dense pillar arrays templates, and by combining the conformal and uniform ALD technique to 'deposit' the TiO_2 pillars other than to 'etch' the TiO_2. A first ALD TiO_2 layer with sufficient thickness was deposited on the Si rods as the framework of the final pillars. After ALD deposition, the wafers were subjected to a short plasma etching to open the top part of the pillars and to remove the TiO_2 on the regions in between the pillars, so that the original Si rods could be exposed to the subsequent etchants. The original Si cores were then removed and refilled by TiO_2. The second ALD deposition not only could fill in those open holes, but also could extend the pillar radius to the desired value. A short TiO_2 etch-back step could be required to isolate the rods from each other and acted as a treatment to improve the quality. In total, only twice short plasma etchings were specially and effectively implemented on TiO_2. The removed thickness was just a little bit more than one forth of the final diameter of the pillars (depending on the thickness of the first ALD TiO_2 films).

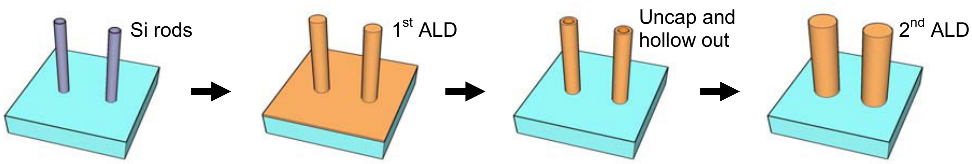

Fig. 2. Process diagram of the AARDE technique.

The nanopillars with the pitch of 1 µm were patterned by ASML PAS 5500/80 stepper and EVG 120. ALD layers were deposited from titanium tetrachloride ($TiCl_4$) and de-ionized water (H_2O) using an ASM F-120 reactor. The deposition was carried out at 300 °C. Cycle length was 7 seconds, including 2 seconds and 3 seconds purge pulses after $TiCl_4$ and water pulse time, respectively. The growth rate of TiO_2 was 0.5 Å/cycle. All etching processes were finished in Trikon Omega 201 ICP etcher. To clarify the possibility of direct shaping of TiO_2, the etch rates of TiO_2 and the selectivity of Si, SiO_2, spr_3012 (PR 1) and spr_3017M (PR 2) compares to TiO_2 were investigated with two ICP etching recipes (Recipe 1 with SF_6 gas flow and high RF power of 125 W; Recipe 2 with SF_6/O_2 gases flow and RF power of 50 W). A Phillips FE-SEM (XL-50) was used to obtain and analyze the structural details in every process steps. The surface roughness of the planar TiO_2 film was studied with an AFM system (NTEGRA platform (NT-MDT)).

3. Results and discussion

To address the difficulty of direct shaping of TiO_2, the etch rates and selectivity data are listed in Table 1. All of the data were obtained from planar films or substrates and with simply open widows of 10 × 10 mm. Although an extremely high power was used in recipe 1, the etch rate of ALD TiO_2 was still much less than Si, PR 1 and PR 2. When exposed to Recipe 2 for fast and anisotropic Si etch,TiO_2 had an even lower etch rate of less than 1 nm/sec, while Si had an average etch rate of 70.0 nm/sec. This study clearly shows that it is really hard to use typical IC-compatible materials as mask layers. At least relevant heights of masking layers (e.g. SiO_2) are required for protecting the patterns. Even in such cases, the anisotropic etching of high and densely spaced TiO_2 pillars is still difficult, since the aspect ratio during etching is at least doubled.

Table 1. Etch rates and selectivity

	TiO_2 etch rate (nm/sec)	Selectivity (compares to TiO_2)			
		Si	SiO_2	PR 1	PR 2
Recipe 1	6.0	6	1	3	3
Recipe 2	< 1	>70	1	4	4

The AARDE process started with the fabrication of 1.78 µm high Si pillars with 1 µm pitch and 145 nm radius by anisotropic plasma etching (Fig. 3 (a), etch rate was 50 nm/sec). The Si pillars are then coated with a 78 nm thick ALD TiO_2 layer (Fig. 3 (b)). After ALD deposition, the wafers are subjected to a 15 seconds plasma etching with Recipe 1 to open the top part of the pillars and to remove the TiO_2 on the regions in between the pillars. The Si cores in the pillars can be clearly seen in Fig. 3 (c).

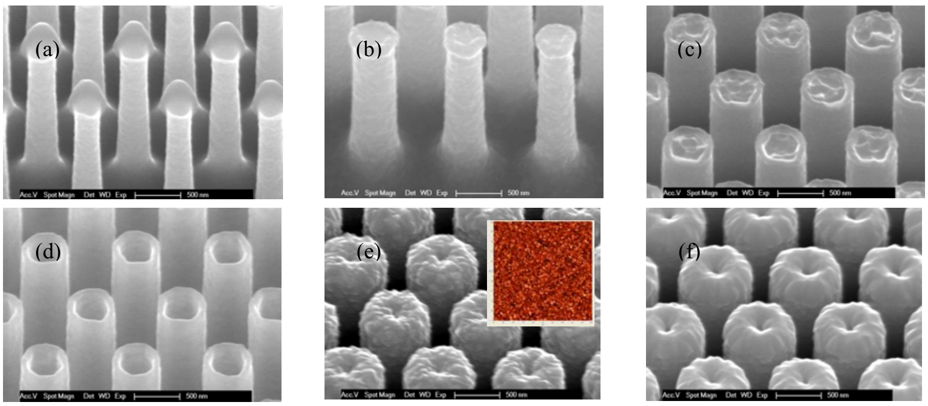

Fig. 3. SEM photos of AARDE process. The inner image shows the AFM picture of 43 nm thick planar TiO_2 film.

The Si inside the cylinders is subsequently etched with Recipe 2, leaving the free standing TiO_2 frameworks (Fig. 3 (d)). No significant height changes were observed before and after the Si core rods removal. When rotating or tilting the sample, the vague outlines of the back pillars could be seen through the transparent TiO_2 cylinders by SEM. A second ALD deposition of 128 nm thick TiO_2 was carried out to refill the opened holes and to extend the pillar radius (Fig. 3 (e)). A gap of about 40 nm was intended to be left in the middle of the pillars for further investigations. It was found that the crystallization effect for the thick ALD TiO_2 layers was so clear that the surface undulation could be easily seen. Our AFM analysis confirmed that the roughness increased with the layer thickness. In samples with 43 nm thick ALD TiO_2 films, crystal grains were also found but the RMS roughness was just 3.3 nm. Indeed, it has been reported that TiO_2 might easily crystallize during deposition. If the film was amorphous, the surface was relatively flat; once the film began to crystallize, the film became rougher and the surface roughness usually increased with deposition temperature and film thickness [4], [9]-[10]. This problem could be solved by adjusting the deposition parameters and/or using post-deposition treatments. Fig. 3 (f) shows for example a plasma treatment. The surface quality of the pillars improved remarkably.

4. Conclusion

An IC-compatible method, called AARDE technique, is presented for photonic crystal sensing applications. The idea is to ‘deposit’ rather than ‘etch’ the rigid materials into pillars. By using such technique, it is easy to fabricate dense arrays of nanosize TiO_2 rods with high aspect. A case study of 1 µm pitch and 1.7 µm high ALD TiO_2 pillar arrays demonstrates the process. Results show that TiO_2 pillars were successfully fabricated from straight Si rods with less direct bombardments on the functional surface, indicating AARDE is a promising technique for nanotechnology and MEMS applications.

Acknowledgements

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References

[1] Joannopoulos JD, Johnson SG, Winn JN and Meade RD. *Photonic crystals: Molding the Flow of Light*. 2nd ed. Princeton: Princeton Univ. Press; 2008.

[2] Macleod HA. Thin-Film Optical Coating Design. In: Flory FR, Editors. *Thin Film for Optical Systems*, New York: Marcell Dekker; 1995, p. 1-40.

[3] Bhattacharyya D, Sahoo NK, Thakur S and Das NC. Spectroscopic ellipsometry of TiO_2 layers prepared by ion-assisted electron-beam evaporation. *Thin Solid Films* 2000; **200**, p. 96-102.

[4] Mardare D. Optical constants of heat-treated TiO_2 thin films. *Mat Sci Eng* 2002; **B95**, p. 83-87.

[5] Norasetthekul S, Park PY, Baik KH, Lee KP, Shin JH and Jeong BS, et al. Dry etch chemistries for TiO_2 thin films. *Appl Surf Sci* 2001; **185**, p. 27-33.

[6] Aarik J, Karlis J, Mandar H, Uustare T and Sammelselg V. Influence of structure development on atomic layer deposition of TiO_2 thin films. *Appl Surf Sci* 2001; **181**, p. 339-348.

[7] Puurunen RL. Surface chemistry of atomic layer depostion: A case study for the trimethylaluminum/water process. *J Appl Phys* 2005; **97**, 121301.

[8] Elam JW, Routkevitch D, Mardilovich PP, George SM. Conformal coating on Ultrahigh-Aspect-Ratio Nanopores of Anodic Alumina by Atomic Layer Deposition. *Chem Mater* 2003; **15**, p. 3507-3517.

[9] Liang S, Chen M, Xue Q, Qi Y and Chen J. Site selective micro-patterned rutile TiO_2 film through a seed layer deposition. *J Colloid Interf Sci* 2007; **311**, p. 194-202.

[10] Mitchell DRG, Triani G, Attard DJ, Finnie KS, Evans PJ, Barbe CJ and Bartlett JR. Atomic layer deposition of TiO_2 and Al_2O_3 thin films and nanolaminates. *Smart Mater Struct* 2006; **15**, p. S57-S64.